

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

# Kinetics and Relative Rates of the Gallium Bromide-Catalyzed Reactions of Alkyl Bromides with Aromatic Hydrocarbons in 1,2,4-Trichlorobenzene Solution<sup>1</sup>

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The gallium bromide-catalyzed reactions of methyl and ethyl bromides with benzene and with toluene in 1,2,4-trichlorobenzene have been studied. The results of the present study indicate that the reactions are first order with respect to each reactant: the aromatic, the alkyl bromide, and the catalyst. The observed values of the third-order rate constant at 18.9° for the ethylation of benzene and toluene are  $2.75 \times 10^{-3}$  and  $17.9 \times 10^{-3} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ , respectively, revealing that ethyl bromide reacts with toluene 6.5 times more rapidly than it does with benzene. For the methylation of benzene and toluene, the third-order rate constants at 25° are  $0.0689 \times 10^{-3}$  and  $0.673 \times 10^{-3} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ , respectively, so that this halide reacts with toluene 9.8 times more rapidly than it does with benzene. The results of the present study are compared with those of previous studies on related reactions and the influence of the solvent on the observed kinetics is considered.

## Introduction

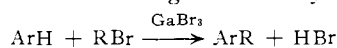
In previous studies on the aluminum bromide-catalyzed reactions of alkyl bromides with benzene and with toluene in 1,2,4-trichlorobenzene as solvent, we observed that the reactions were first order with respect to each reactant: the aromatic, the alkyl bromide, and the catalyst.<sup>3</sup> We also observed that the gallium bromide-catalyzed alkylations of benzene and toluene, in the aromatic as solvent, were second order with respect to the catalyst.<sup>4-6</sup> Thus, quite different kinetics were evident in these two closely related alkylation reactions.

The available results did not permit a decision as to whether the difference in the observed kinetics was a consequence of the different catalysts used or a consequence of the presence of 1,2,4-trichlorobenzene as a solvent in the aluminum bromide-catalyzed alkylation.

It appeared of interest, therefore, to study the gallium bromide-catalyzed alkylation in 1,2,4-trichlorobenzene in order to establish which of these two factors was responsible for the marked difference in the observed kinetics.

## Results

**Ethylation of Benzene and Toluene.**—In a previous paper<sup>6</sup> we described an experimental technique for following the kinetics of the Friedel-Crafts alkylation reactions of aromatic hydrocarbons, based on measurements of the pressure of the hydrogen bromide liberated by the reactions in a high vacuum system.



By application of that method, we were able to study the kinetics of the reactions of ethyl bromide with benzene and with toluene in 1,2,4-trichlorobenzene under the influence of gallium bromide. Typical data obtained at 18.9° are shown graphically in Fig. 1, where the logarithm of  $(P_\infty - P_0)/(P_\infty - P)$  is plotted against time. The symbols  $P_0$ ,  $P$ , and  $P_\infty$  denote the total pressure of the system observed at the time zero,  $t$ , and infinity (*i.e.*, after the completion of the reactions), respectively. Since the first-order rate constant,  $k_1$ , can be expressed by the equation

$$k_1 = \frac{2.303}{t} \log \frac{P_\infty - P_0}{P_\infty - P}$$

the linear relationships observed between the logarithm of  $(P_\infty - P_0)/(P_\infty - P)$  and the time indicate that the reactions are first order with respect to the alkyl bromide at the given initial concentrations of gallium bromide and the aromatic hydrocarbon.

(1) The Catalytic Halides. XXVII.

(2) Post-doctorate Research Associate (1956-1957) on Project No. AT(11-1)-170 supported by the Atomic Energy Commission.

(3) H. Jungk, C. R. Smoot, and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 2185 (1956).

(4) C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6245 (1956).

(5) C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6249 (1956).

(6) S. U. Choi and H. C. Brown, *ibid.*, **81**, 3315 (1959).

The aromatics were used in excess over the alkyl bromide during the course of each kinetic run. Also the kinetic observations were limited to only the initial stages of the reactions. Hence, the amount of the aromatics in the reaction mixtures remained almost constant during the course of each kinetic study.

Thus, the gallium bromide-catalyzed reactions of ethyl bromide with benzene and with toluene in 1,2,4-trichlorobenzene follow first-order kinetics with respect to the alkyl bromide at the given initial concentrations of the aromatic and the catalyst. A series of kinetic runs was, therefore, made to determine the effect, if any, of the initial concentrations of the aromatic and the catalyst. The data are summarized in Table I. The values of the third-order rate constant,  $k_3$ , were obtained by dividing these values of  $k_1$  by the product of initial concentrations of the aromatic and gallium bromide. The reasonable constancy of  $k_3$  values obtained indicates that the reactions are first order with respect to each reactant: the aromatic, the alkyl bromide, and the catalyst.

$$\text{rate} = k_3[\text{ArH}][\text{GaBr}_3][\text{RBr}]$$

The average values of  $k_3$  at 18.9° for the ethylation of benzene and of toluene are  $2.75 \times 10^{-3}$  and  $17.9 \times 10^{-3} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ , respectively, leading to a toluene/benzene reactivity ratio,  $k_T/k_B$ , of 6.5 for the reaction of the aromatics with ethyl bromide at 18.9° in 1,2,4-trichlorobenzene.

TABLE I

RATE CONSTANTS FOR THE GALLIUM BROMIDE-CATALYZED REACTION OF ETHYL BROMIDE WITH BENZENE AND TOLUENE IN 1,2,4-TRICHLOROBENZENE AT 18.9°

Aromatic	Concn., mole/l.			$10^3 k_1$ , sec. <sup>-1</sup>	$10^3 k_3$ , $\text{l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$
	ArH	GaBr <sub>3</sub>	EtBr		
Benzene	1.72	0.0356	0.179	0.178	2.91
	0.657	.0362	.212	.0735	3.09
	4.06	.0192	.208	.178	2.28
	0.941	.0107	.121	.0273	2.71
				Av.	2.75 <sup>a</sup>
	0.886	0.0212	0.315	0.0453	2.41 <sup>b</sup>
Toluene	1.65	.0201	.133	.549	16.6
	2.35	.0208	.125	.900	18.4
	1.43	.00772	.0662	.205	18.6
				Av.	17.9 <sup>a</sup>
		1.40	0.0222	0.231	0.161

<sup>a</sup> Reactivity ratio,  $k_T/k_B = 6.5$ . <sup>b</sup> The reaction was followed by the standard titrimetric method. <sup>c</sup> Hydrogen bromide (1.845 mmoles) was added to the system prior to the initiation of the reaction (GaBr<sub>3</sub>, 0.187 mmole).

**Methylation of Benzene and Toluene.**—It was of interest to extend the study to the methylation of benzene and toluene under the same experimental conditions. Accordingly, we attempted to apply the

manometric technique to a determination of the kinetics of the methylation reaction. Unfortunately, the method proved to be inconvenient for this reaction, mainly because of the much lower rates. Therefore, the gallium bromide-catalyzed reactions of methyl bromide with benzene and with toluene in 1,2,4-trichlorobenzene were studied at 25°, utilizing simple titrimetric determination<sup>4</sup> of hydrogen bromide. Typical data for the studies are represented in Fig. 2, where the values of  $\log a/(a-x)$  are plotted against time. The symbols  $a$  and  $x$  denote the number of moles of the methyl bromide introduced originally, and of the hydrogen bromide liberated at time  $t$ , respectively. The data indicate that the methylation reaction is also first order with respect to the alkyl bromide at the given initial concentrations of the catalyst and the aromatic.

A series of kinetic runs was made to determine the effect of the initial concentrations of the aromatic and the catalyst. The data are summarized in Table II. The relative constancy of the third-order rate constant,  $k_3$ , indicates that the reactions are first order with respect to each reactant, as in the ethylation reaction. The average values of  $k_3$  at 25° for the methylation of benzene and toluene are  $0.0689 \times 10^{-3}$  and  $0.673 \times 10^{-3} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ , respectively, leading to a toluene/benzene reactivity ratio,  $k_T/k_B$ , of 9.8 for the reaction of these aromatics with methyl bromide at 25° in 1,2,4-trichlorobenzene.

TABLE II

RATE CONSTANTS FOR THE GALLIUM BROMIDE-CATALYZED REACTIONS OF METHYL BROMIDE WITH AROMATICS IN 1,2,4-TRICHLOROBENZENE AT 25°

Aromatic	Concn., mole/l.			$10^3 k_1$ , sec. <sup>-1</sup>	$10^3 k_3$ , l. <sup>2</sup> mole <sup>-2</sup> sec. <sup>-1</sup>
	ArH	GaBr <sub>3</sub>	MeBr		
Benzene	1.80	0.0458	0.334	0.617	0.0748
	1.80	.0241	.334	.260	.0599
	0.991	.0241	.214	.172	.0720
	Av.				.0689 <sup>a</sup>
Toluene	1.87	0.0458	0.399	5.92	.691
	1.17	.0241	.399	1.90	.674
	0.654	.0241	.273	1.03	.654
	Av.				.673 <sup>a</sup>

<sup>a</sup> Reactivity ratio,  $k_T/k_B = 9.8$ .

### Discussion

The results clearly indicate that the markedly different kinetics discussed earlier must arise from the use of 1,2,4-trichlorobenzene as a solvent in the one study,<sup>3</sup> but not in the other,<sup>4</sup> and not to any difference in the mode of operation of the two catalysts—gallium bromide *vs.* aluminum bromide.

It is of interest to compare the results of the present study with those of the previous studies<sup>3-6</sup> on related Friedel-Crafts alkylation reactions and to consider further possible explanations for the observed kinetics. The available data are summarized in Table III. For ready comparison, the rate constants for the gallium bromide-catalyzed reactions of ethyl bromide with benzene and with toluene at 25° have been estimated from the values observed at 18.9°. This estimation was made by assuming that the entropy of activation for the gallium bromide-catalyzed ethylation of benzene is the same as the corresponding values for the related reactions involving aluminum bromide<sup>7</sup> and by assuming that the toluene/benzene reactivity ratio,  $k_T/k_B$ , for the reactions at 25° is not significantly different from the value at 18.9°.<sup>7</sup>

(7) We have observed remarkable constancy in the entropy of activation terms for the alkylation of aromatics (ref. 3), as well as for other aromatic substitution reactions.

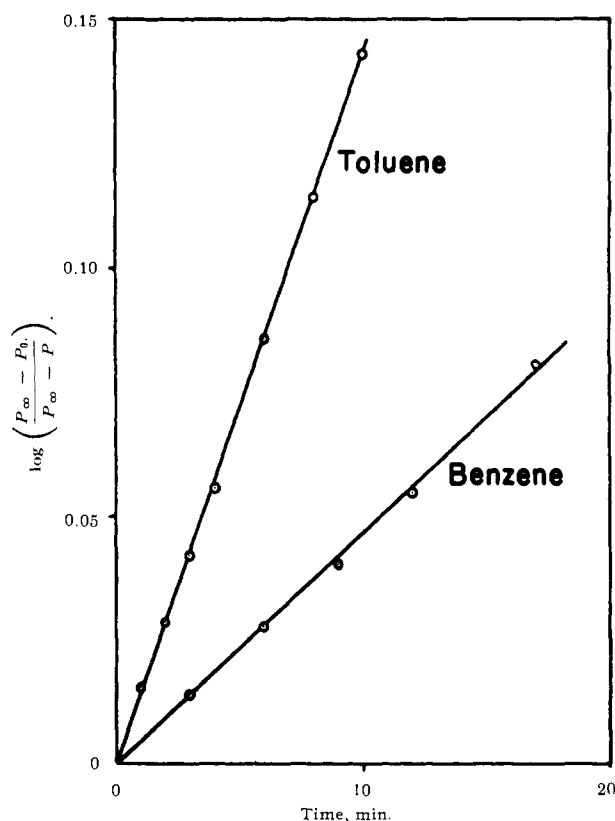


Fig. 1.—Rate data for the gallium bromide-catalyzed reaction of ethyl bromide with aromatics in 1,2,4-trichlorobenzene at 18.9°.

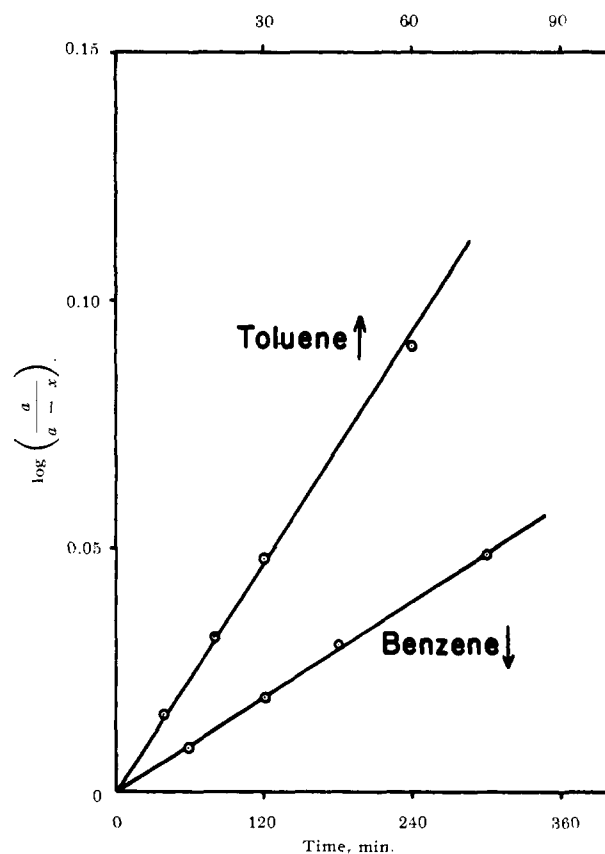


Fig. 2.—Rate data for the gallium bromide-catalyzed reaction of methyl bromide with aromatics in 1,2,4-trichlorobenzene at 25°.

The data summarized in Table III reveal significant differences in the various reactions. First, it is seen that the gallium bromide-catalyzed reactions are slower

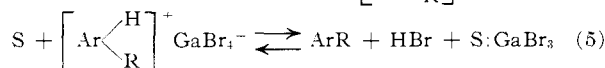
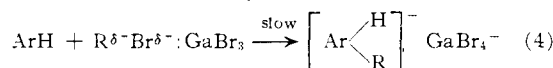
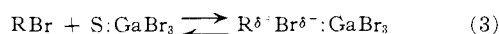
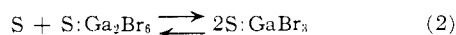
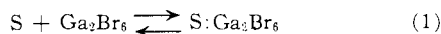
TABLE III  
RATE CONSTANTS FOR THE REACTIONS OF ALKYL BROMIDES WITH AROMATICS UNDER THE INFLUENCE OF GALLIUM AND ALUMINUM BROMIDES AT 25°

Catalyst	RBr	ArH	Kinetics <sup>a</sup>	In 1,2,4-C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>			In excess ArH			
				10 <sup>3</sup> k <sub>3</sub> <sup>b</sup>	1.2 mole <sup>-2</sup> sec. <sup>-1</sup>	k <sub>T</sub> /k <sub>B</sub>	Ref.	Kinetics <sup>a</sup>	1.2 mole <sup>-1</sup> sec. <sup>-1</sup>	k <sub>T</sub> /k <sub>B</sub>
GaBr <sub>3</sub>	MeBr	Benzene	3rd order	0.0689	9.8	<sup>e</sup>	2nd order	0.00500	5.7	<sup>a</sup>
		Toluene	3rd order	0.673		<sup>e</sup>	2nd order	.0285		<sup>a</sup>
	EtBr	Benzene	3rd order	4.3 <sup>d</sup>	6.5	<sup>e</sup>	2nd order	.159	2.5	<sup>a</sup>
		Toluene	3rd order	28 <sup>d</sup>		<sup>e</sup>	2nd order	.392		<sup>a</sup>
<i>i</i> -PrBr	Benzene					2nd order	320	1.8	<sup>h</sup>	
	Toluene					2nd order	580		<sup>h</sup>	
AlBr <sub>3</sub>	MeBr	Benzene	3rd order	3.58	5.1	<sup>f</sup>				
		Toluene	3rd order	18.3		<sup>f</sup>				
	EtBr	Benzene	3rd order	227	2.9	<sup>f</sup>				
		Toluene	3rd order	653		<sup>f</sup>				
<i>i</i> -PrBr	Benzene		>10 × 10 <sup>3</sup>		<sup>f</sup>					

<sup>a</sup> The kinetics established are shown. <sup>b</sup> Rate = k<sub>3</sub>[ArH][MBr<sub>3</sub>][RBr]. <sup>c</sup> Rate = k<sub>2</sub>[GaBr<sub>3</sub>]<sup>2</sup>. <sup>d</sup> Estimated from the experimental values at 18.9°. <sup>e</sup> The present study. <sup>f</sup> Reference 3. <sup>g</sup> References 4 and 5. <sup>h</sup> Reference 6.

than the corresponding reactions under the influence of aluminum bromide, indicating that gallium bromide is a milder Friedel-Crafts catalyst than aluminum bromide. This might be related to the observation that in the presence of hydrogen bromide, gallium bromide forms less stable  $\sigma$ -complexes with aromatic hydrocarbons than does aluminum bromide.<sup>8</sup> Second, Table III indicates that the methylation reactions in each system are much slower than the corresponding ethylation reactions. Finally, Table III reveals that the toluene/benzene reactivity ratio,  $k_T/k_B$ , for the slower alkylation reactions is greater than the corresponding value for the faster reactions of any given set under similar conditions. For example, the value of  $k_T/k_B$ , 9.8, for the gallium bromide-catalyzed methylation reaction in 1,2,4-trichlorobenzene is greater than the value, 6.5, for the ethylation reaction under the same conditions. Furthermore, these two values are greater than the respective values, 5.1 and 2.9, obtained for the corresponding reactions under the influence of aluminum bromide.

As a result of the present study, it must be concluded that the solvent used plays an important role in the observed reaction kinetics. The experimental observations for the reactions in 1,2,4-trichlorobenzene appear to be in accord with the reaction mechanism proposed below (S = 1,2,4-trichlorobenzene).



This mechanism leads to the kinetic expression

$$\text{rate} = k_3[ArH][S:Ga_2Br_6][RBr]$$

In step 3 we postulate the formation of a polarized alkyl bromide-gallium bromide addition compound,  $R^{\delta+}Br^{\delta-}:Ga_2Br_6$ .<sup>9</sup> The breaking of the carbon-bromine bond in the alkyl bromide is considered to contribute in an important way to the stability of the transition state of the reaction.<sup>6</sup> The experimental observation that the methylation reaction is slower than the ethylation reaction under similar reaction conditions is in agreement with the ability of the alkyl group to tolerate a positive charge.

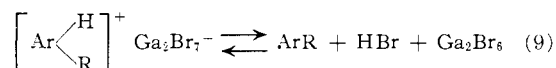
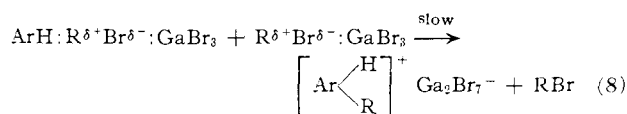
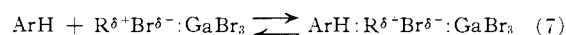
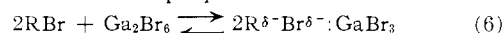
(8) S. U. Choi and H. C. Brown, paper in preparation.

(9) An ion-pair intermediate,  $R^+Ga_2Br_4^-$ , could also be postulated. For further discussion see reference 3.

Step 4, the formation of a  $\sigma$ -complex, is assumed to be the rate-determining step of the reaction. Then, the fact that gallium bromide is a milder catalyst than aluminum bromide could be explained in terms of the relative ability for  $\sigma$ -complex formation of the two metal bromides.<sup>8</sup>

In a previous paper<sup>6</sup> it was suggested that the bond making by the aromatic must be considered to contribute in a less important way to the stability of the transition state than the breaking of the carbon-bromine bond of the alkyl bromide. However, the bond making by the aromatic appears to become more significant in the slower reactions, resulting in a greater value of  $k_T/k_B$  than in the faster reactions.

For the reaction in excess aromatics, the following reaction mechanism is proposed.



In step 7 we postulate that a  $\pi$ -complex is formed between an aromatic molecule and the positive end of the polarized alkyl bromide-gallium bromide addition compound. Step 8, the formation of a  $\sigma$ -complex, is assumed to be the rate-determining step of the reaction also in this system. However, the  $\sigma$ -complex is assumed to be formed through the interaction of the alkyl bromide-gallium bromide addition compound with the  $\pi$ -complex mentioned above, instead of with the aromatic molecules themselves. This mechanism then leads to the kinetic expression

$$\text{rate} = k_2[ArH][RBr:Ga_2Br_6]^2$$

According to this interpretation, the coordinating ability of the solvent, 1,2,4-trichlorobenzene, plays a dominant role in altering the kinetics from those observed in the hydrocarbon system to those observed in the 1,2,4-trichlorobenzene system.

### Experimental

**Materials.**—All the materials used were purified as described previously.<sup>3-6</sup>

**Kinetic Measurements Utilizing the Manometric Technique.**—The manometric procedure employed for kinetic measurements inside a high vacuum system was described in a previous paper of this series.<sup>6</sup> Data of a typical run are summarized in Table IV.

The validity of the experimental procedure used for following the kinetics in the present study had been tested previously in

TABLE IV

DATA FOR THE GALLIUM BROMIDE-CATALYZED REACTION OF ETHYL BROMIDE WITH BENZENE IN 1,2,4-TRICHLOROBENZENE AT 18.9°<sup>a</sup>

Time, min.	Pressure, mm.	$\log \left( \frac{P_\infty - P_0}{P_\infty - P} \right)$	$10^3 k_t$ , sec. <sup>-1</sup>
0	27.20	....	...
3	30.20	0.0140	0.178
6	32.95	.0273	.175
9	35.55	.0400	.170
12	38.35	.0546	.175
17	43.10	.0803	.182
25	50.15	.121	.185
∞	111.60	....	...
			Av. 0.178

<sup>a</sup> ArH = 9.026 mmoles, GaBr<sub>3</sub> = 0.187 mmole, EtBr = 0.939 mmole, C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub> = 6.926 g.

experiments utilizing excess aromatic as the solvent.<sup>6</sup> In other words, the values of the rate constants for the gallium bromide-catalyzed reactions of methyl and ethyl bromides with toluene at low temperatures, determined by the present experimental technique in a high vacuum system, agreed closely with the values calculated from the rate constants<sup>5</sup> obtained at higher temperatures by standard kinetic methods utilizing titration techniques. In order to establish the validity of the manometric technique for systems containing 1,2,4-trichlorobenzene, the reaction in this solvent of ethyl bromide with benzene under the influence of gallium bromide was also studied at 18.9° by the standard titrimetric determination of hydrogen bromide. The results provided a value of  $2.41 \times 10^{-3}$  l.<sup>2</sup> mole<sup>-2</sup> sec.<sup>-1</sup> for the third-order rate constant for the reaction (Table I). This value agrees fairly well with the average value obtained above by the kinetic measurement with the manometric technique. Therefore, it is concluded that any errors arising from the assumptions involved in the pressure technique for the kinetic studies appear to be no greater than the experimental error.

**Kinetic Measurements by Titrimetric Determination of Hydrogen Bromide.**—The procedure for kinetic measurements by the

titrimetric determination of hydrogen bromide was reported previously.<sup>3</sup> Data of a typical run are summarized in Table V.

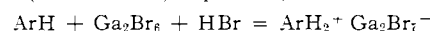
TABLE V

DATA FOR THE GALLIUM BROMIDE-CATALYZED REACTION OF METHYL BROMIDE WITH BENZENE IN 1,2,4-TRICHLOROBENZENE AT 25°<sup>a</sup>

Time, min.	Base, ml.	$\log \left( \frac{a}{a-x} \right)$	$10^3 k_t$ , sec. <sup>-1</sup>
0	9.350	....	...
60	9.820	0.00903	0.578
120	10.350	.0195	.623
180	10.880	.0302	.643
300	11.780	.0489	.625
			Av. .617

<sup>a</sup> ArH = 1.80 moles/l., GaBr<sub>3</sub> = 0.0458 mole/l., MeBr = 0.334 mole/l.

In the present study, a rapid decrease in rate was observed in the latter stages of each run of the experiment, as was observed previously in the related reactions.<sup>3-6</sup> The decrease in rate was faster than any reasonable order would predict. In the hope of clarifying the reason for the rapid decrease in rate, the effect of the added hydrogen bromide on the rate was examined. The gallium bromide-catalyzed reaction of ethyl bromide with toluene in 1,2,4-trichlorobenzene was started after the addition of hydrogen bromide and followed by the present pressure technique. The observed third-order rate constant at 18.9° was  $5.18 \times 10^{-3}$  l.<sup>2</sup> mole<sup>-2</sup> sec.<sup>-1</sup> (Table I). This value is much smaller than the corresponding value obtained without the addition of hydrogen bromide. Thus the addition of hydrogen bromide retards the reaction. The decrease in rate is attributed to the decrease in effective concentration of the catalyst due to the formation of  $\sigma$ -complexes of gallium bromide-hydrogen bromide with aromatics (reactant and/or product).



Consequently, only kinetic data in the initial stages of the alkylation reactions were utilized for the determination of the rate constants in both the manometric and titrimetric procedures (Tables IV and V).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON STATE UNIVERSITY, PULLMAN, WASH.]

## Neighboring Boron in Nucleophilic Displacement<sup>1a</sup>

BY DONALD S. MATTESON AND RAYMOND W. H. MAH<sup>1b</sup>

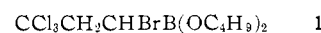
RECEIVED APRIL 1, 1963

Displacement of bromide ion from the  $\alpha$ -haloalkaneboronic ester, dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate, by nucleophiles such as iodide, butoxide, and butyl mercaptide ion is greatly facilitated by the neighboring boron atom. Butoxide evidently attacks the boron atom first to form the tetravalent boron anion, which then rearranges with expulsion of bromide ion. Strong support for this mechanism is furnished by the behavior of butyl B-aryl- and B-alkyl-B-(1-bromo-3,3,3-trichloro-1-propyl)-boronates, which upon mild base treatment expel bromide ion with migration of the B-aryl or B-alkyl group from boron to carbon.

### Introduction

Neighboring-group effects of metallic atoms have not been studied extensively with the exception of elimination reactions. Elimination of a metal cation, often coordinated with a base, together with a halide ion or other leaving group from an  $\alpha$ -,<sup>2</sup>  $\beta$ -,<sup>3</sup> or  $\gamma$ -position<sup>4</sup> often proceeds so readily that it excludes all other possible reactions. However, if the carbon-metal

bond is strong enough, attack of a nucleophile on an  $\alpha$ -haloalkylmetallic compound may result in displacement of halide ion. Trimethylsilylmethyl chloride behaves in this fashion, apparently with some facilitation of attack of iodide ion by a vacant d-orbital of silicon.<sup>5,6</sup> The familiar example of such neighboring-group activation occurs in  $\alpha$ -halocarbonyl compounds.<sup>6,7</sup> These are closely related to the present series of boron compounds, boronic and carboxylic acids being iso-electronic. Investigation of the reactivity of  $\alpha$ -haloalkylboron compounds was made possible by the availability of dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate (1) from dibutyl ethyleneboronate and bromotrichloromethane.<sup>8</sup>



(1) (a) Supported by National Science Foundation Grant G 19906. (b) National Science Foundation Cooperative Predoctoral Fellow, 1961-1962; abstracted in part from the Ph.D. thesis of R. W. H. M.

(2) Examples include the reaction of iodomethylzinc iodide with olefins (H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959)) and the formation of *t*-butylmethylene from phenylsodium and neopentyl chloride (L. Friedman and J. G. Berger, *ibid.*, **83**, 492, 500 (1961)).

(3) Among numerous examples are: debromobromination, B. M. Mikhailov and P. M. Aronovich, *Izvest. Akad. Nauk SSSR, Otd. Khim. Nauk*, 927 (1961); *Chem. Abstr.*, **55**, 24541 (1961); desilicochlorination, L. H. Sommer, L. J. Tyler, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948); and deoxymercuration, M. M. Kreevoy and G. B. Bodem, *J. Org. Chem.*, **27**, 4539 (1962), and references cited therein.

(4) An example is cyclopropane formation by debromochlorination, M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 1886 (1960).

(5) C. Eaborn and J. C. Jeffrey, *J. Chem. Soc.*, 4266 (1954).

(6) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

(7) P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, **80**, 5808 (1958).

(8) D. S. Matteson, *ibid.*, **82**, 4228 (1960).